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⑤④ **Metallized porous fluorinated resin and process therefor.**

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**Description****BACKGROUND OF THE INVENTION**

5 Porous fluorinated polymer materials that have numerous fine pores have been known for sometime. Further, the formation of a metal film through chemical plating (nonelectrolytic plating) on the surface inside the pores in these materials is also known, as shown in Japanese patent publication 60-500905, and U.S. patents 3,235,473 (LeDuc), 3,383,247 (Adihart, et al), 4,204,918 and 4,348,429 (McIntyre, et al), 4,557,957 and 4,720,400 (Manniso).

10 According to this known technology, materials with a metal film on the surfaces inside the resin pores are manufactured through a series of steps in which first a porous fluorinated resin material is immersed in a water-soluble surfactant solution to fill the voids in the pores of the resin with the surfactant solution. Then a step is carried out in which the surfactant solution contained in the pores is replaced with an aqueous solution of a palladium/tin activator so that palladium is deposited onto the surface inside the pores. Then the solution  
15 inside these pores is replaced with hydrochloric acid, the hydrochloric acid inside these pores is replaced with a wash bath, and finally the material that has been thus treated is immersed in a chemical plating bath and subjected to chemical plating.

In this conventional method, when the material is taken out after being immersed in the water-soluble surfactant solution, there is a great decrease in the hydrophilicity of the inside surfaces of the pores, and when  
20 the inside surfaces of the pores are dried, these pore surfaces become water repellant, thereby making it difficult to fill the pores with the aqueous solution used in the next step. Consequently, with this conventional method, the aqueous solution contained in the pores must be subjected to a liquid-liquid replacement with the aqueous solution used in the following step in order to prevent the drying of the inside surfaces of the pores and fill the pores with the aqueous solution.

25 However, such methods involving numerous liquid-liquid replacement operations require precise control over the time, temperature, and pressure in order to accomplish the liquid-liquid replacement, and the inconvenience of these operations is a major drawback.

The present invention solves the above problems evident in the prior art by providing a method for efficiently forming a metal film on the surface inside of the pores in a porous fluorinated polymer material, as well  
30 as the porous fluorinated polymer outside surfaces with a metal film that is obtained with this method.

**SUMMARY OF THE INVENTION**

35 The present invention comprises the discovery that when a hydrophilic polymeric coating is bonded to the inside surface of the pores of a porous fluorinated polymer material and this product is then used as the material to be plated in a chemical plating treatment, there is no need for the liquid-liquid replacement operations entailed in the above conventional methods. A metal film can be formed efficiently on the surface inside of the pores by conducting chemical plating with standard methods.

40 The present invention provides a porous fluorinated polymer material that has a metal film, which is characterized by the fact that in a porous fluorinated resin material that has numerous fine pores with an average pore diameter of 100  $\mu\text{m}$  or less, a metal film is formed over a hydrophilic polymeric film on the surfaces of the pores of said polymer.

45 The present invention also offers a process for manufacturing a porous fluorinated polymer that has a metal film, characterized by the fact that after first forming a hydrophilic polymeric film on the surfaces of the pores of a porous fluorinated polymer that has numerous fine pores with an average pore diameter of 100  $\mu\text{m}$  or less, a chemical plating treatment is performed.

**DESCRIPTION OF THE INVENTION**

50 The porous fluorinated polymer used as the substrate in the present invention may be any such substance that has continuous pores with an average pore diameter of 100 microns or less. The means for forming these pores is not particularly restricted, and drawing, expansion, foaming, extraction, or other such known means may be employed. Neither are there any particular restrictions placed on the type of fluorinated resin, with the use of all types being possible. The fluorinated polymer preferred in the present invention is polytetrafluoroethylene, but in addition to this, copolymers of tetrafluoroethylene and hexafluoropropylene, polyvinyl fluoride,  
55 polyvinylidene fluoride, and the like can also be used.

The porous fluorine polymer material most preferred as the substrate in the present invention comprises drawn or expanded polytetrafluoroethylene, which has an average pore diameter of 100 microns or less, pre-

ferably, 50 microns or less, and a porosity of 15 to 95%, preferably 50 to 95%. Such a substrate is discussed in detail in Japanese Patent Publication 56-45773 and 56-17216 and U.S. Patent 4,187,390.

Various types of polymers that have hydrophilic groups can be used in the present invention as the hydrophilic polymer to be bonded inside the pores of the porous fluorinated resin material. Examples of hydrophilic groups include hydroxyl groups, carboxyl groups, sulfone groups, cyano groups, pyrrolidone groups, isocyanate groups, imidazole groups, phosphoric acid groups, N-substitutable amide groups, N-substitutable amino groups, and sulfonamide groups. Also, an alkylene oxide such as ethylene oxide or propylene oxide may be subjected to an addition reaction with the active hydrogen in these hydrophilic groups.

The hydrophilic polymer may be water soluble, but if it is, it will be difficult to adequately maintain the polymer until the chemical plating process is begun once it has been bonded to the inside of the pores in the material, which can lead to the dissolving and removal of the polymer in the pre-treatment process for the chemical plating, thereby precluding the maintenance of adequate hydrophilicity on the inside surface of the pores. Consequently, the hydrophilic polymeric substance that is used would be one that exhibits solubility with respect to water and aqueous solutions and preferably one that is essentially insoluble in water.

The hydrophilic polymer can be a polyvinyl alcohol, polyacrylic acid, polyacrylonitrile, polyvinyl sulfone, polyurethane, polyethylene oxide, starch, carboxymethyl cellulose, ethyl cellulose, sodium alginate, gluten, collagen, casein, and various other synthetic and natural polymeric substances that have hydrophilicity, but particularly from the standpoint of bondability with the fluorinated resin, the use of a hydrophilic polymer that contains fluorine is advantageous. Such a fluorine-containing hydrophilic polymer can be obtained by copolymerizing an ethylenic unsaturated monomer that contains fluorine with a vinyl monomer that contains hydrophilic groups but does not contain fluorine. Examples of fluorine-containing monomers include tetrafluoroethylene, vinyl fluoride, vinylidene fluoride, chlorotrifluoroethylene, dichlorodifluoroethylene, and hexafluoropropylene. A desirable fluorine-containing monomer is the one expressed by the general formula  $CXY:CFZ$ , where Z is fluorine or hydrogen and X and Y are selected from among hydrogen, fluorine, chlorine, and trifluoromethyl ( $-CF_3$ ). Other desirable fluorine-containing monomers are those expressed by the general formula  $CH_2:CRCO_2R_f$ ,  $CH_2:CROR_f$ ,  $CH_2:CRCONHR_f$ , where R is hydrogen, fluorine, a methyl group, an ethyl group, a trifluoromethyl group ( $CF_3$ ), or pentafluoroethyl ( $C_2F_5$ ).  $R_f$  is a perfluoroalkyl group with 4-21 carbons. Preferred monomers containing hydrophilic groups are the above vinyl monomers that have hydrophilic groups, as well as monomers in which an alkylene oxide such as ethylene oxide or propylene oxide has been subjected to an addition reaction with the active hydrogen in these groups. Those that yield copolymers containing hydrophilic groups by performing first copolymerization and then hydrolysis, such as vinyl acetate, are also used.

Specific examples of these hydrophilic monomers include vinyl alcohol, acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid, and other such unsaturated carboxylic acids, as well as alkylene oxide adducts of acrylic acid or methacrylic acid, such as  $CH_2:CRCO_2(C_2H_4O)_mH$ ,  $CH_2:CRCO_2(C_3H_6O)_nH$ ,  $CH:CRCO_2(C_3H_6O)_m(CF_2H_4O)_nH$ , and  $CH_2:CRCONH(CN_2)_3NH_2$  in which R is hydrogen or a methyl group and n and m are integers greater than or equal to one.

Both the fluorine-containing monomer and the monomer containing hydrophilic groups may be used singularly or in combinations of two or more. And if needed, other vinyl monomers, such as alkyl esters or acrylic acid or methacrylic acid, esters of trimethylolpropane or other such polyhydric alcohols and acrylic acids or methacrylic acids and the like can also be used jointly with the above fluorine-containing monomer and the monomer containing hydrophilic groups.

The copolymer of a vinyl alcohol and a fluorine-containing monomer that can be used as a desirable hydrophilic polymeric substance in the present invention can be obtained by subjecting a copolymer of vinyl acetate and a fluorine-containing monomer to saponification, and then converting the acetate groups contained in the copolymer into hydroxyl groups. In this case, not all of the acetate groups contained in the copolymer necessarily have to be converted into hydroxyl groups. Instead, the conversion of the acetate groups into hydroxyl groups may be performed to the extent that the copolymer becomes hydrophilic.

The percent fluorine in the preferred fluorine-containing hydrophilic copolymer is normally 2 to 60% by weight and preferably 10 to 60%, with 20 to 60% being most preferred. If the fluorine-containing hydrophilic copolymer contains too much fluorine, the heat resistance will be good, but the hydrophilicity of the copolymer will be diminished. On the other hand, if the fluorine content is too low, the adhesion of the fluorine-containing hydrophilic copolymer to the fluorinated polymer will be low, and its heat resistance will be poor.

In the fluorine-containing hydrophilic copolymer used preferably in the present invention, the hydrophilic group equivalent thereof is generally 45 to 700, with 60 to 500 being preferable and 60 to 450 being most preferable. When the hydrophilic group equivalent is less than 45, the solubility of the fluorine-containing hydrophilic copolymer will be extremely high, so that the copolymer will readily dissolve out of the fluorinated polymer in water and, conversely, if the hydrophilic group equivalent is greater than 700, the hydrophilicity will be so

low that the objective of making the fluorinated polymer hydrophilic cannot be achieved.

Tables 1 and 2 show for several different copolymers the molar percentage of fluorine-containing monomer units in the copolymers, the fluorine weight percentage (F-wt %), and the hydrophilic group equivalent (Eq-W). VOH indicates vinyl alcohol.

The hydrophilic equivalent (Eq-W) referred to in this specification is a value obtained by dividing the molecular weight of the copolymer by the number of hydrophilic groups. The hydrophilic group equivalents given below were calculated with the equation  $\text{Eq-W} = (A \cdot x + B \cdot y) y$ .

In the equation,  $A \cdot x$  is a value obtained by multiplying the molecular weight of the fluorine-containing copolymer by the molar number  $x$  thereof, while  $B \cdot y$  is a value obtained by multiplying the molecular weight of the copolymer containing hydrophilic groups by the molar number  $y$  thereof.

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TABLE 1

Copolymer	Molar Ratio in the Copolymer	Molar % of Fluorine-containing Monomer Units in the Copolymer	F-wt%	Eq-W
$(CF_2:CF_2)_x(VOH)_y$	x=1, y=40	2.4	4.2	45.5
	1, 30	3.2	5.5	46.4
	1, 20	4.8	7.9	48.0
	1, 10	9.1	14.3	53
	1, 4	20	27.5	68
	1, 1	50	53.1	143
$(CF_2:CH_2)_x(VOH)_y$	10, 1	91	72.8	1043
	x=1, y=40	2.4	2.1	44.6
	1, 30	3.2	2.8	45.2
	1, 20	4.8	4.1	46.2
	1, 10	9.1	7.5	49
	1, 4	20	-	-
$(CFH:CH_2)_x(VOH)_y$	1, 1	50	33.6	107
	10, 1	91	55.6	683
	x=1, y=40	2.4	1.1	44.2
$(CFH:CH_2)_x(VOH)_y$	1, 30	3.2	1.4	45.6
	1, 20	4.8	2.1	45.3
	1, 10	9.1	4.0	47.6
	1, 4	20	-	-
	1, 1	50	21.3	89
	10, 1	91	37.8	503

TABLE 2

Copolymer	Molar Ratio in the Copolymer	Molar % of Fluorine-containing Monomer Units in the Copolymer		F-wt%	Eq-W
$(CF_2:CFCL)_x(VOH)_y$	x=1, y=40	2.4	3.1	46.0	
	1, 30	3.2	4.0	46.9	
	1, 20	4.8	5.8	48.9	
	1, 10	9.1	10.4	54.6	
	1, 4	20	-	-	
	1, 1	50	35.8	159	
25	10, 1	91	47.2	1208	
$(CF_2:CCL_2)_x(VOH)_y$	x=1, y=40	2.4	2.0	46.6	
	1, 30	3.2	2.7	47.7	
	1, 20	4.8	3.8	50.0	
	1, 10	9.1	6.7	57	
	1, 4	20	-	-	
	1, 1	50	20.8	183	
35	10, 1	91	26.3	1442	
$(CF_2:CF_2CF_3)_x(VOH)_y$	x=1, y=40	2.4	6.1	46.8	
	1, 30	3.2	7.9	48.0	
	1, 20	4.8	11.3	50.5	
	1, 10	9.1	19.6	58	
	1, 4	20	-	-	
	1, 1	50	59.0	193	
45	10, 1	91	73.9	1543	

In order to bond the hydrophilic polymer to the inside surface of the pores in the fluorinated porous polymer, the copolymer is dissolved in an alcohol, a ketone, an ester, an amide, a hydrocarbon or other such organic solvent.

The hydrophilic polymer is either immersed in this solution or the solution is sprayed on or applied with a roller to impregnate the fluorinated polymer with the solution and the solution is then dried. By so doing, the hydrophilic polymers are bonded to the inside surfaces of the fluorinated polymer, thereby permitting water

to penetrate into the fine pores. The amount of hydrophilic polymer substance bonded to the fluorinated polymer should be an amount that is sufficient to enhance the hydrophilicity of the fluorinated polymer and while this amount will vary depending on the porosity of the fluorinated polymer and other factors, it is normally 1.5 to 10 wt % and preferably 2 to 6 wt % by weight of the final product.

The hydrophilic porous fluorinated polymer can also be manufactured by impregnating it with an organic solvent solution of a copolymer composed of a fluorinated monomer and a hydrophobic monomer that can be converted into hydrophilic groups (such as vinyl acetate), drying the fluorinated polymer, and then converting at least part of the acetate groups to hydrophilic groups.

The shape of the porous fluorinated polymer used in the present invention is discretionary. The material can be in the form of a film, tape, tube, yarn, fiber, fabric, rod, or rope for example.

The hydrophilic porous fluorinated polymer obtained in the above manner will have a structure in which the hydrophilic polymer substances are bonded to the inside surface of the material. This structure allows water and various aqueous solutions to penetrate and permeate into the pores. By setting the hydrophilic group equivalent of the hydrophilic polymer to within an appropriate range and controlling the solubility of the polymer with respect to water, the elution of the polymer itself from the material can be prevented. The bonding strength of the fluorine-containing hydrophilic copolymer with the porous fluorinated polymer is heightened through the action of the fluorine atoms in the copolymer, so that the durability thereof can be maintained in a stable state over extended periods of time.

In the present invention, a porous fluorinated polymer treated with the hydrophilic polymer is used as the raw material to be subjected to a chemical plating pre-treatment and a chemical plating treatment. Both of these treatments can be carried out according to conventional methods.

Specifically, in the pre-treatment step, a precious metal that serves as the catalyst in the chemical plating is bonded to the inside surface of the pores onto the hydrophilic polymer. Palladium, platinum, gold, or the like can be used as this precious metal, with palladium being preferable. For the bonding of this metal, a method can be employed in which, for example, the hydrophilic treated porous polymer is first subjected to an aqueous solution of tin(II) chloride then washed with water and immersed in an aqueous solution of palladium chloride and washed again with water. When the hydrophilic polymer bonded to the porous fluorinated polymer is one that has amino groups, carboxyl groups, chlorine, or other such precious metal ion scavenging groups, a method can also be employed in which the treated polymer is first immersed in an aqueous solution containing the precious metal ions and then washed with water. These pretreatments for chemical plating are well known techniques.

The treated porous fluorinated polymer that has thus undergone the pre-treatment is then subjected to a chemical plating treatment by being immersed in a chemical plating bath.

The chemical plating bath will generally contain a metal, a reducing agent, a complexing agent, a buffer, a stabilizer, and the like. Here, sodium hypophosphite, sodium borohydride, aluminoborane, formalin, hydrazine, and the like can be used as the reducing agent, and formic acid, acetic acid, succinic acid, citric acid, tartaric acid, malic acid, glycine, ethylenediamine, EDTA, triethanolamine, potassium sodium tartrate, and the like can be used as the complexing agent and the buffer.

Examples of plating metals include gold, silver, platinum, rhodium, nickel, cobalt, tungsten, copper, zinc, iron, and various other metals, as well as alloys of these. To obtain an alloy metal film, metal salts with a composition that corresponds to the desired metal film should be used as the metal salts added to the plating bath.

In order to form a metal film of platinum or gold or an alloy thereof, or other metal film that is difficult to form through chemical plating on the hydrophilic polymer used in the present invention, a metal film which can be easily formed through chemical plating, such as cobalt, nickel, or copper, is first formed on the hydrophilic polymer, and this polymer then subjected to a chemical plating treatment or electroplating treatment.

When chemical plating is used to form a metal film compound of platinum or an alloy containing platinum on the hydrophilic polymer used in the present invention, the chemical plating treatment can be facilitated through the use of hydrazine hydrochloride as the reducing agent. Since the reduction of the platinum ions in a chemical plating bath that contains platinum ions occurs readily, it is difficult to selectively deposit the platinum on only the object being plated, but when hydrazine hydrochloride is used as the reducing agent, there is a marked increase in the stability of the plating bath, thereby allowing the platinum to be selectively deposited on only the object being plated. Further, when hydrazine hydrochloride is used as the reducing agent, a metal film of a platinum alloy, such as platinum-iridium or platinum-rhodium, can be easily obtained.

A composite plating method can also be employed for the chemical plating method used in the present invention. This composite plating method is one in which a metal film is formed that contains a micropowder of an oxide, nitride, or carbide of a metal, for example, and the plating bath is one in which this micropowder has been uniformly dispersed.

In the present invention, since a porous fluorinated polymer to which a hydrophilic polymer has been bond-

ed is used as the raw material to be plated, a metal film can be easily formed on the inside surface of the pores of this material through chemical plating. Naturally, in the present invention, the metal film can be formed not only on the inside surface of the pores, but also over the entire surface of the material. For instance, with a sheet material, the metal film can be formed inside the pores and on one side of the sheet, or inside the pores and on both sides of the sheet. For those portions of the material surface on which no metal film formation is desired, a plastic material, such as a polytetrafluoroethylene film or other plastic film, can be used to cover those portions prior to the chemical plating, and this plastic film is then peeled off after the chemical plating. The thickness of the metal film formed in the chemical plating is normally approximately 10 Å to 1 µm and in particular 500 Å to 4000 Å.

With the present invention, the metallized polymer film that has been obtained in the above manner can also be subjected to further chemical plating or electroplating and a porous metal film can be formed on the surfaces thereof.

The metallized porous fluorinated polymer of the present invention is characterized in that it has a metal film (is metallized) on at least the inside surface of the pores thereof and this metal film is bonded to the polymer via the hydrophilic polymer. When the porous fluorinated polymer is one that has a fine structure that includes knodes in which fibers are bonded together, such as the one described in Japanese Patent Publication 56-17216, the metal film essentially encloses these knodes and fibers.

With the present invention, the thickness of the fluorinated polymer can be suitably controlled using a method in which the porous fluorinated polymer is coated with the hydrophilic polymer, a method in which the porous fluorinated polymer is impregnated with various types of aqueous solutions, or a similar method. Examples of this finished product include; a sheet that is conductive along the sheet thickness direction and one or both surfaces of the sheet; a sheet that is conductive only on both surfaces of the sheet; a sheet that is conductive only on one surface of the sheet; a tube that is conductive along the tube thickness direction and one or both surfaces of the tube; a tube that is conductive only on both surfaces of the tube; and a tube that is conductive only on one surface of the tube.

The present invention can provide a metallized porous fluorinated polymer that has a platinum film. Because of its fine porosity, this material has a large specific surface area, so that it can be used as a platinum electrode with a large reaction surface area. Furthermore, since such a platinum electrode is pliant and tough, the electrode can be formed into different shapes at will, thereby allowing the electrolysis tank to be made more compact. And this electrode has the advantage that only a small amount of expensive platinum is used. In addition, by combining this electrode with solid electrolysis, smaller electric cells, capacitors, and other such chemical elements can be obtained.

The present invention can provide a highly efficient gas diffusion electrode by laminating a porous fluorinated polymer sheet over metallized polymer sheet that has a platinum film. Gas diffusion electrodes are generally porous electrodes in which one side is in contact with electrolyte and the other side is in contact with a reaction gas. On the inside of the gas diffusion electrode is formed a three-phase interface of the electrode, the reaction gas, and the electrolyte. In addition to chemical resistance and corrosion resistance, gas diffusion electrodes must also have a function that prevents the leakage of electrolyte on the reaction gas side and the bubbling of the reaction gas to the electrolyte side.

By positioning the side of the metallized polymer that has the platinum film on the electrolyte side and the porous fluorinated polymer sheet that is not metallized on the reaction gas side, the laminate of the present invention, composed of the metallized polymer that has a platinum film and the porous fluorinated polymer sheet, can serve as an ideal gas diffusion electrode, which was unattainable by prior art methods.

The present invention also offers a laminate that is generally composed of metallized polymer that has a platinum film and a porous fluorinated polymer sheet. In addition to being used as a gas diffusion electrode as mentioned above, since such a laminate is conductive and has excellent hydrophilicity on one side and is insulating and has excellent hydrophobicity on the other side, it can also be used in a wide variety of fields in which its characteristics can be utilized.

Because the metallized polymer of the present invention is hydrophilic and conductive, it can be used to advantage as a conductive filtration membrane, a sensor membrane, an electromagnetic shield, a catalyst material, a conductive clothing material, a flexible printed substrate or an antenna material.

The metallized polymer of the present invention can be used in many different shapes, such as sheet, tube, wire, cable, rod, yarn, fiber, fabric or a cylinder.

## EXAMPLES

The present invention will now be described in further detail by giving practical examples.



Experimental ProcedureThickness

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The thickness was measured with a dial thickness gauge with a precision of 1/1000 mm.

Ethanol Bubble Point (EBP)

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Ethanol was spread over the surface of the material (film) sample, the sample placed horizontally on a fixing apparatus, and the EBP measured. Here, air was blown from below the sample. The EBP is the initial pressure (kg/cm<sup>2</sup>) at the point air bubbles are continuously exiting from the surface on the reaction side. The average pore diameter can be calculated from the EBP by a method such as ASTM-F316-80, wherein the pore size is obtained by an instrument, Model No. "PORO" (Cutler Electronics Ltd.). The pore size distribution curve for a sample sheet is automatically obtained by the instrument. The integrated curve is divided by 2 to obtain the average pore diameter.

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Porosity

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The porosity of the polymer film prior to impregnation was obtained by measuring the density of the material. The density of the material (polytetrafluoroethylene) was 2.2 g/cm<sup>3</sup>. The porosity was calculated using the equation:

$$\text{Porosity} = (2.2 - \text{sample density}) \div 2.2 \times 100$$

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In the calculation of the porosity after impregnation, a density of 2.1 g/cm<sup>3</sup> was used in place of the 2.2 g/cm<sup>3</sup>.

Flow Time

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The flow time is the amount of time required for 200 ml of water to pass through a sample with a diameter of 35 mm under a vacuum of one atmosphere. The sample was fixed horizontally and water was poured over it. A vacuum was then applied from below. When measuring a sample before impregnation, the sample was first impregnated with ethanol to make the material hydrophilic.

Durability

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The durability of the material after the impregnation treatment is an indication of its hydrophilicity after undergoing five Flow Time tests and being dried after each test, or after ten liters of water had passed through using a flow test machine and method.

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Fluorine and Hydroxyl Group Content

The fluorine content and the hydroxyl group content were determined through calculation.

Water Permeability (WP)

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The WP was determined with the equation:

$$\text{WP} = 200 \div (\text{flow time} \div 60 \times (1.75)^2 \times 3.14)$$

Heat Resistance

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The heat resistance was determined by fixing the film in a frame, leaving the film in an air oven controlled to the test temperature, and then measuring the hydrophilicity in the manner given below.

Gurley Number (GN)

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The GN was determined by measuring the amount of time required for 100 cubic centimeters of air to pass through a sample with a surface area of 6.45 cm<sup>2</sup> under a water pressure of 12.4 cm.

**Acid, Alkali, and Solvent Resistance**

The sample was immersed in a solution for the length of time given in the practical examples, then, after drying, its hydrophilicity was measured in the manner given below.

**Hydrophilicity**

The initial hydrophilicity was determined by dropping a drop of water onto the sample from a height of 5 cm, then measuring the time needed for the water drop to be absorbed. The hydrophilicity was evaluated in the following manner:

- A. absorbed in one second or less;
- B. absorbed eventually;
- C. absorbed only under pressure;
- D. no absorption, but reduction in the water drop contact angle; and
- E. no absorption, that is the water was repelled (this E evaluation is characteristic of porous fluorine resin material)

**Reference Example 1**

A copolymer of tetrafluoroethylene and a vinyl alcohol (a saponified copolymer of tetrafluoroethylene and a vinyl acetate (degree of saponification of 100%, fluorine content 27 wt. %, hydroxyl group content 14.5 mmol/g) was dissolved in one liter of methanol to prepare a 0.2 wt. % methanol solution. A porous fluorinated resin film with a thickness of 40 microns and a porosity of 80% was immersed in and impregnated with this methanol solution, fixed in a frame, and dried at 60°C for five minutes. This same process was repeated five times to obtain a hydrophilic porous film whose hydrophilicity received an A rating and whose flow time was 60 seconds. The thickness of this film was 30 microns, its porosity was 70%, its EBP was 1.2 kg/sq. cm., its calculated pore diameter was 0.2 microns, and its WP was 20 cm<sup>3</sup>/cm<sup>2</sup>/minute. This good hydrophilicity was still evident after 24 hours at a heat resistance temperature of 120°C, but the hydrophilicity was lost at 135°C.

Upon immersing this film in water, no elution of the hydrophilic copolymer into the water occurred. Neither was any change observed upon immersion in boiling water. This film exhibited a high level of acid resistance with respect to 12 N hydrochloric acid at room temperature and 1 N hydrochloric acid at 80°C, and to other such acids, and also exhibited a high level of alkali resistance with respect to 5 N sodium hydroxide at room temperature and 1 M sodium hydroxide at 80°C, and to other such alkalies.

**Reference Example 2**

A copolymer of tetrafluoroethylene and vinyl acetate was dissolved in methyl ethyl ketone to prepare a 0.5 wt % solution. A porous polytetrafluoroethylene film with a thickness of 40  $\mu$ m and a porosity of 80% was impregnated with this solution, fixed in a frame, and dried at 60°C for five minutes. This same process was repeated five times. The film thus obtained was saponified by immersing it in ethanol containing sodium methoxide and then heat treating it for 30 minutes. This saponified hydrophilic film was then washed with water. This film displayed the same characteristics as the film in Reference Example 1.

**Reference Comparative Example 1**

A porous, expanded polytetrafluoroethylene film with a thickness of 40  $\mu$ m and a porosity of 80% was impregnated for 20 minutes with a 5 wt % isopropanol solution of an anionic surfactant (ammonium perfluoroalkyl sulfonate) (FC-93, made by 3M) that served as a surfactant and was then dried at room temperature to produce a hydrophilic film. This film had poor stability and its hydrophilicity was lost after 200 ml of water had been passed through the film five times.

**Reference Example 3**

A porous polytetrafluoroethylene, with a thickness of 48  $\mu$ m, a GM of 6.1 seconds, an EBP of 1.15 kg/cm<sup>2</sup>, a porosity of 76%, and a flow time of 36 seconds, was immersed for 30 seconds in a 1% solution of the copolymer used in Reference Example 1, after which the film was taken out, fixed in a frame, and dried at room temperature for one hour. The properties of the film thus obtained were as follows: copolymer content in the film 0.75 kg/m<sup>2</sup>, film thickness 39  $\mu$ m; GN 10.4 seconds; EBP 1.2 kg/cm<sup>2</sup>; porosity 71%; flow time 56 seconds;

WP speed 20 cm<sup>3</sup>/m<sup>2</sup>/minute.

Hydrophilicity and durability tests were performed after either passing 200 ml of water through an impregnated film (drying after each time) (Method 1) or passing 10 l. of water through continuously (Method 2). The results were as follows:

#### Durability Test Conditions

#### Hydrophilicity Test Results

10	Method 1	A
	Method 2	A

15 An impregnated film was subjected to a five-time flow time test. Drying was performed after each test. Upon then subjecting this film to a hydrophilicity test, it had an A rating. For another impregnated film, a flow time test machine and test method were used to pass 10 l. of water through the film continuously. The hydrophilicity test result for this film had an A rating.

20 To determine the heat resistance, an impregnated film was first subjected to a heat treatment at the temperatures and for the durations given below and then to a hydrophilicity test, whereupon the following results were obtained:

	<u>Temperature</u>	<u>Duration</u>	<u>Hydrophilicity Test Results</u>
25	100°C	30 hours	A
	120°C	6 hours	B(absorption after 60 sec.)
	120°C	24 hours	B(absorption after 60 sec.)
	120°C	48 hours	B(absorption after 120 sec.)
30	150°C	2 hours	C or D
	150°C	24 hours	D
	200°C	1 hour	D

35 Another sample of the impregnated membrane was immersed under the following oxidative conditions for the following times and the hydrophilicity test was then carried out with the following results:

	<u>Oxidative Agent</u>	<u>Temperature</u>	<u>Time</u>	<u>Hydrophilicity Test Results</u>
40				
45	2N-HNO <sub>3</sub>	85°C	2 hr.	A
	3N-HNO <sub>3</sub>	R.T.	350 hr.	A

Hydrophilicity after immersion for 350 hours in 3N-HNO<sub>3</sub> at room temperature was A.

50 Hydrophilicity after immersion for 2 hours in 2N-HNO<sub>3</sub> at -85°C was A.

To determine oxidation resistance, after immersing an impregnated film under the oxidation conditions shown below for the durations shown below, a hydrophilicity test was conducted which gave the following results:

55

	<u>Oxidant</u>	<u>Temperature</u>	<u>Duration</u>	<u>Hydrophilicity Test Results</u>
	1 N hydrochloric acid	80°C	2 hours	A
5	3 N nitric acid	room temperature	350 hours	A
	12 N nitric acid	room temperature	1 hour	A

- 10 After immersing an impregnated film under the alkaline conditions shown below for the durations shown below, a hydrophilicity test was conducted which gave the following results:

	<u>Alkali</u>	<u>Temperature</u>	<u>Duration</u>	<u>Hydrophilicity Test Results</u>
15	1 N sodium hydroxide	80°C	2 hours	A
	1 N sodium hydroxide	80°C	5 hours	D
	6 N sodium hydroxide	room temperature	36 hours	A

- 20 After passing the solvents shown below through an impregnated film, a hydrophilicity test was conducted to obtain the following results.

	<u>Solvent</u>	<u>Flow-through Amount</u>	<u>Hydrophilicity Test Results</u>
25	Methanol	300 ml	A
	Ethanol	2000 ml	A
	Acetone	5000 ml	A

- 30 Even though methanol is a good solvent of the copolymer, the hydrophilicity rating was A after 300 ml of methanol had been passed through the film. Ethanol and acetone are not good solvents of the above-mentioned copolymer.

### 35 Practical Example 1

A porous fluorinated polymer film (a circle of polytetrafluoroethylene film with a diameter of 50 mm) that had a thickness of 40 microns, a porosity of 80%, and a pore diameter of 0.2 microns, was degreased and cleaned by immersing it in acetone for five minutes.

- 40 Two weight parts of a copolymer of tetrafluoroethylene and a vinyl alcohol (a saponified copolymer of tetrafluoroethylene and vinyl acetate, with a degree of saponification of 100%, a fluorine content of 27 wt %, and a hydroxyl group content of 14.5 mmol/g) was dissolved in one liter of methyl alcohol.

This solution was used to impregnate the above film that had been degreased and cleaned and, after drying for five minutes at 60°C, the film was immersed in water.

- 45 This film was then immersed for two minutes at room temperature in an aqueous solution of tin(II) chloride ( $\text{SnCl}_4$ ) that had been made acidic with hydrochloric acid, thereby causing the tin ions to be adsorbed onto the surface of the film and the film was washed with water. This film was then immersed for two minutes at room temperature in an acidic aqueous solution of palladium chloride ( $\text{PdCl}_2$ ) to bring about the precipitation of a small amount of palladium on the surface of the film and the film was washed with water.

- 50 After this, the film was immersed for one minute in an organic electrolytic nickel plating bath (Ni-20I, made by Kojundo Kagaku Kenkyusho) that was maintained at 80°C and the porous fluorine resin film was plated with nickel. The thickness of the plating that surrounded the knots and fibers at this point was approximately 100 Å.

### 55 Practical Example 2

A porous fluorinated polymer film (a circle of polytetrafluoroethylene film) with a diameter of 50 mm that had a thickness of 40 microns, a porosity of 80%, and a pore diameter of 0.2 microns) was degreased and cleaned by immersing it in acetone for five minutes.

Two weight parts of a copolymer of tetrafluoroethylene and a vinyl alcohol (a saponified copolymer of tetrafluoroethylene and vinyl acetate, with a degree of saponification of 100%, a fluorine content of 27 wt %, and a hydroxyl group content of 14.5 mmol/g) was dissolved in one liter of methyl alcohol. This solution was used to impregnate the above film that had been degreased and cleaned, and after drying for five minutes at 80°C, the film was immersed in water.

This film was then immersed for two minutes at room temperature in an aqueous solution of tin(II) chloride ( $\text{SnCl}_4$ ) that had been made acidic with hydrochloric acid, thereby causing  $\text{Sn}^{2+}$  to be adsorbed onto the surface of the film and the film was washed with water. This film was then immersed for two minutes at room temperature in an acidic aqueous solution of palladium chloride ( $\text{PdCl}_4$ ) to bring about the precipitation of a small amount of palladium on the surface of the film and the film was washed with water.

This film was then plated with platinum by immersing it for 120 minutes at 40°C in a plating bath for which 0.26 g of chloroplatinic acid hexahydrate had been added to 100 ml of an aqueous solution in which 0.9 g of hydrazine hydrochloride had been dissolved. The thickness of the plating that surrounded the knots and fibers at this point was approximately 1000 Å and the amount of precipitation was 2 mg/cm<sup>2</sup>.

### Practical Example 3

The nickel-plated, fine, porous polytetrafluoroethylene material obtained in Practical Example 1 was immersed for 30 minutes in a non-electrolytic gold plating bath (K-24N, made by Kojundo Kagaku Kenkyusho) maintained at 85°C, thereby gold plating the nickel-plated, fine, porous polytetrafluoroethylene material. The thickness of the plating that surrounded the knots and fibers at this point was approximately 3000 Å, and therefore, the total thickness of the nickel plating and the gold plating was approximately 4000 Å.

### Claims

1. A metallized fluorinated polymer comprising:
  - (a) porous fluorinated polymer having an average pore diameter of 100 microns or less;
  - (b) a hydrophilic polymer film, comprising a copolymer of a fluorinated monomer and a monomer containing hydrophilic groups, coated on at least the inside pore surface of said fluorinated polymer; and
  - (c) at least one layer of metal film coating the hydrophilic polymer film surfaces inside said pores of said porous fluorinated polymer.
2. A polymer of Claim 1 wherein said fluorinated polymer comprises porous expanded polytetrafluoroethylene.
3. A polymer of Claims 1 or 2 wherein said metal film comprises a multi-layer metal film.
4. A process for manufacturing a metallized fluorinated polymer comprising the steps of:
  - (a) coating at least the inside surface of a porous fluorinated polymer having an average pore diameter of 100 microns or less with a hydrophilic polymer film comprising a copolymer of a fluorinated monomer and a monomer containing hydrophilic groups; and
  - (b) coating the surface of said hydrophilic polymer film with at least one layer of metal film.

### Patentansprüche

1. Metallisiertes fluoriertes Polymer, welches umfaßt:
  - (a) ein poröses fluoriertes Polymer mit einem durchschnittlichen Porendurchmesser von 100 µm oder weniger;
  - (b) einen hydrophilen Polymerfilm, der ein Copolymer aus einem fluorierten Monomer und einem Monomer umfaßt, das hydrophile Gruppen enthält, der auf mindestens einer Innenoberfläche der Poren des fluorierten Polymers aufgebracht ist; und
  - (c) mindestens eine Schicht eines Metallfilms, der die Oberflächen des hydrophilen Polymerfilms in den Poren des porösen fluorierten Polymers bedeckt.
2. Polymer nach Anspruch 1, worin das fluorierte Polymer ein poröses gedehntes Polytetrafluorethylen umfaßt.

3. Polymer nach Anspruch 1 oder 2, worin der Metallfilm einen mehrschichtigen Metallfilm umfaßt.
4. Verfahren zur Herstellung eines metallisierten fluorierten Polymers, welches die Schritte umfaßt:
  - (a) Beschichtung mindestens einer Innenoberfläche eines porösen fluorierten Polymers mit einem durchschnittlichen Porendurchmesser von 100 µm oder weniger mit einem hydrophilen Polymerfilm, der ein Copolymer eines fluorierten Monomers und eines Monomers umfaßt, das hydrophile Gruppen enthält; und
  - (b) Beschichtung der Oberfläche des hydrophilen Polymer films mit mindestens einer Schicht eines Metallfilms.

#### Revendications

1. Polymère fluoré métallisé, comprenant :
  - (a) un polymère fluoré poreux ayant un diamètre moyen de pore de 100 microns ou moins ;
  - (b) un film de polymère hydrophile, comprenant un copolymère d'un monomère fluoré et d'un monomère à groupes hydrophiles, déposé au moins sur la surface intérieure des pores de ce polymère fluoré ; et
  - (c) au moins une couche d'un film métallique recouvrant les surfaces du film de polymère hydrophile à l'intérieur des pores de ce polymère fluoré poreux.
2. Polymère selon la revendication 1, dans lequel le polymère fluoré comprend du polytétrafluoroéthylène expansé poreux.
3. Polymère selon la revendication 1 ou 2, dans lequel le film métallique comprend un film métallique à plusieurs couches.
4. Procédé de fabrication d'un polymère fluoré métallisé, selon lequel :
  - (a) on revêt au moins la surface intérieure d'un polymère fluoré poreux ayant un diamètre moyen de pore de 100 microns ou moins, avec un film de polymère hydrophile comprenant un copolymère d'un monomère fluoré et d'un monomère à groupe hydrophile ; et
  - (b) on revêt la surface de ce film de polymère hydrophile avec au moins une couche de film métallique.

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HYDROPHILIZED POLYOLEFIN POROUS FILM AND SEPARATOR FOR BATTERY

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### Claims

1. A hydrophilized polyolefin porous film characterized by the following facts: the porous film is made of a polyolefin resin; in the structure viewed from the cross section of the porous film with an average pore size in the range of 0.05-5  $\mu\text{m}$  and a porosity of 50-85%, elliptical pores are layered randomly, and the number of layered elliptical pores present on the cross section in parallel with the maximum strength direction (layer density in the thickness direction) is 20 or more; the inner surfaces of the pores of the porous film are covered by a surfactant.
2. The hydrophilized polyolefin porous film described in Claim 1 characterized by the fact that the surfactant is at least one type selected from polyoxyethylene alkyl ethers, polyoxyethylene alkylphenol ethers, fatty acid monoglycerides, and aliphatic amine salts.
3. A separator for batteries made of the hydrophilized polyolefin porous film described in Claim 1.

### Detailed explanation of the invention

#### Industrial application field

The present invention pertains to a hydrophilized polyolefin porous film which can be used as a separator for electrolytic capacitors, electric double-layer capacitors, Li batteries, etc., and to a separator for batteries using the aforementioned porous film.

#### Prior art

Examples of hydrophilized porous films include the hydrophobic porous (polyolefin) film hydrophilized by covering part of or the entire inner surface of the pores of the hydrophobic film with polyethylene glycol (Japanese Kokai Patent Application No. 59[1974]-24732) and the hydrophilized hydrophobic film with a porosity in the range of 20-90 vol% and having at least part of the surfaces of the pores covered by a propylene glycol mono fatty acid ester (Japanese Kokai Patent Application No. 61[1986]-71803).

#### Problems to be solved by the invention

It is conventionally preferred to use a solvent with a high boiling point, such as propylene carbonate,  $\gamma$ -butyrolactone, or sulfolane, as the electrolyte of electrolytic capacitors and Li batteries. These solvents with a high boiling point, however have a surface tension as high as 30-40 dyne/cm. Therefore, the conventional hydrophilized porous films have poor wettability (impregnability) with respect to such electrolyte. Also, since the electrolyte retaining property is poor, the equivalent serial resistance (ESR) becomes high. In addition, since the coating film

adhesion between the surfactant and the porous film is poor, the surfactant tends to enter the electrolyte to diminish the hydrophilization effect.

The purpose of the present invention is to solve the aforementioned problems by providing a hydrophilized polyolefin porous film which can display excellent wettability with respect to electrolyte as well as excellent electrolyte retaining property when used as a separator for batteries and has strong coating film adhesion so that it is difficult for the surfactant to enter the electrolyte.

#### Means to solve the problems

In order to realize the aforementioned purpose, the present invention provides a hydrophilized polyolefin porous film characterized by the following facts: the porous film is made of a polyolefin resin; in the structure viewed from the cross section of the porous film with an average pore size in the range of 0.05-5  $\mu\text{m}$  and a porosity of 50-85%, elliptical pores are layered randomly, and the number of layered elliptical pores present on the cross section in parallel with the maximum strength direction (layer density in the thickness direction) is 20 or more; the inner surfaces of the pores of the porous film are covered by a surfactant. The present invention also provides a separator for batteries made of the aforementioned porous film.

The polyolefin resin used in the present invention is the polymer or copolymer of ethylene, propylene, butene-1, methylbutene, methylpentene, or other  $\alpha$ -olefins. Among them, it is preferred to use a homopolymer with excellent crystallinity and high stereoregularity. However, if necessary, it is also possible to graft polar monomers in order to improve the electrolyte impregnability.

The melting point of the polyolefin is preferably 130°C or higher in consideration of the heat in the soldering or manufacturing process of an element. The more preferable melting point of the polyolefin of 150°C allows a virtually problem-free, normal processing. When the glass transition temperature ( $T_g$ ) of the resin is 10°C or lower, cracking at low temperatures will be reduced. Therefore, polypropylene is preferred among the polyolefin resins. It is particularly preferred to use polypropylene with an intrinsic viscosity  $[\eta]$  in the range of 1.5-3.5 dL/g, more preferably, in the range of 2.1-3.3, most preferably, in the range of 2.1-3.0 and having an isotactic index of 93% or higher for its excellent solvent resistance and mechanical properties.

The average pore size of the hydrophilized porous film disclosed in the present invention should be in the range of 0.05-5  $\mu\text{m}$ , preferably, in the range of 0.1-3  $\mu\text{m}$ .

If the average pore size is too small, the ESR change rate will increase due to the viscosity of the electrolyte. For example, when the viscosity of the electrolyte rises due to the change-over time (so-called dry-up), the ESR will increase significantly to cause problems in use. On the other hand, if the average pore size is too large, movement of fine electroconductive

substances cannot be prevented. As a result, the leakage current will increase, or short circuits will occur.

The porosity of the porous film disclosed in the present invention should be in the range of 50-85%, preferably, in the range of 60-75%. If the porosity is lower than 50%, since the amount of retained electrolyte is not sufficient, the ESR will increase due to dry-up. On the other hand, if the porosity is higher than 85%, the mechanical characteristics will be degraded. The frequency of occurrence of pinholes caused by foreign substances will increase, and the possibility of short circuiting also increases.

In the structure viewed from the cross section of the porous film disclosed in the present invention, elliptical pores are layered randomly, and the number of layered elliptical pores present on the cross section in parallel with the maximum strength direction (layer density in the thickness direction) must be 20 or more, preferably, in the range of 25-50. If the layer density in the thickness direction is less than 20, since the amount of retained electrolyte is not sufficient, the ESR will increase due to dry-up. On the other hand, if there is no special limitation on the upper limit of the layer density in the thickness direction, the mechanical characteristics will be degraded significantly, and the possibility of short circuiting will increase when the aforementioned density is more than 250.

If the elliptical pores (empty pores) are layered randomly in the structure viewed from the cross section of the porous film, they can be covered in a wandering fashion when the film is immersed in the surfactant. Since the pores are layered in the thickness direction, an excellent coating film adhesion to the base material (durability) can be realized.

In the present invention, the surfactant used for hydrophilizing the aforementioned porous film by being coated on the inner surfaces of the pores of the porous film can be a nonionic surfactant or a cationic surfactant. The nonionic surfactant is preferred in consideration of its electrical characteristics. Among the nonionic surfactants, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenol ethers, and fatty acid monoglycerides are particularly preferred because they have good adhesion to the base material of the porous film and affinity (impregnability) with respect to electrolyte and have no adverse effect on the battery's performance. In this case, the number of additional moles of polyoxyethylene is preferably in the range of 4-40. Hexyl groups having 6 carbon atoms or dodecyl groups having 12 carbon atoms are preferably used as the alkyl group in consideration of the adhesivity, affinity (impregnability), and handling property. Also, stearic acid having 18 atom carbons or erucic acid having 22 carbon numbers is preferably used as the fatty acid for the fatty acid monoglyceride due to the reason described above.

Among the cationic surfactants, aliphatic amine salts are preferred. The diethanolamine of lauric acid or oleic acid is particularly preferred in consideration of the adhesivity, affinity,

stability, and handling property. The aforementioned surfactants can be used either alone or as a mixture of several types.

In the present invention, in order to hydrophilize the porous film by coating a surfactant on the inner surface of the pores of the porous film, the surfactant is first dissolved in an organic solvent. It is preferred to use an organic solvent with a low boiling point, such as methanol, ethanol, ethyl acetate, methyl ethyl ketone, etc. The aforementioned porous film can be immersed in this solution, or the solution can be coated or sprayed on the porous film. Then, the porous film is dried under heating at a temperature (conventionally around 100°C), at which the solvent can be evaporated.

After the surfactant is immersed, sprayed, or coated, the porous film can also be stretched monoaxially, biaxially, or multiaxially. The amount of surfactant attached to the porous film (weight base) is conventionally in the range of 2-30%, preferably, in the range of 7-20%. If the amount of surfactant is too small, the hydrophilization effect will not be increased to a certain level. On the other hand, if the amount of surfactant is too large, the pores may be blocked.

The liquid paraffin passing time of the hydrophilized porous film disclosed in the present invention is preferably 5 sec or less, more preferably, in the range of 0.5-3 sec so that both good ESR and mechanical characteristics can be obtained.

The rupture strength of the porous film of the present invention in the length direction is preferably 1.5 kg/15 mm or higher, more preferably, 1.8 kg/15 mm or higher so that good element [illegible; possibly, flexibility] can be realized.

When used as a separator, the thickness of the porous film of the present invention is preferably less than 50  $\mu\text{m}$ , more preferably, in the range of 10-40  $\mu\text{m}$  so that good electric characteristics and mechanical characteristics can be obtained.

Also, when the heat shrinkability at 120°C of the porous film of the present invention is less than 9%, especially, less than 7%, deterioration of the electric characteristics over time caused by seaming of the element can be prevented.

The method to be described below is the most preferred method for manufacturing the hydrophilized porous film of the present invention. It, however, is not the only choice.

First, the polyolefin porous film can be manufactured as follows. 80-240 parts by weight, preferably, 100-200 parts by weight of a phthalate, phosphate or other organic solid used as a plasticizer for vinyl chloride, such as dicyclohexyl phthalate (DCHP) or triphenyl phosphate (PP), are added to 100 parts by weight of a polyolefin resin. After the mixture is melt-extruded, a good solvent for the organic solid, such as trichloromethane, trichloroethane, acetone, methyl ethyl ketone, ethyl acetate, methanol, toluene, or xylene, is used to extract 95% or more, preferably, 98% or more of the aforementioned organic solid.

In this case, in order to randomly layer elliptical holes in the structure viewed from the cross section of the porous film and to have 20 or more layered elliptical pores on the cross section, the melt-extrusion temperature is lowered to about 210°C. When the mixture is molded into a film shape or tube shape, it is drawn at a draft ratio of 6 or higher, preferably, 8 or higher and is cooled for solidification and wound at a temperature higher than the melting point of the organic solid but lower than the melt crystallization temperature of the polyolefin resin. Then, a roll type stretcher or a stenter type stretcher is used to stretch the film 1.5-8 times at least monoaxially at a temperature higher than the glass transition temperature of the polyolefin but lower than the melting point - 10°C. In this way, the porous film of the present invention can be obtained. The porous film is immersed in a solution prepared by dissolving a surfactant in an organic solvent, followed by drying. As a result, the hydrophilized porous film of the present invention is obtained.

The porous film manufactured in this way can display excellent characteristics when used as a separator for batteries. Also, since the porous film of the present invention has a uniform pore size and excellent mechanical characteristics, it can also be used as an excellent microfilter.

#### Effects of the invention

According to the present invention, when a polyolefin porous film with specified average pore size, porosity, and layer density in the thickness direction is immersed in a surfactant to coat the surfactant on the inner surfaces of the pores, a porous film with excellent wettability with respect to electrolyte and excellent electrolyte retaining property as well as excellent coating film adhesivity (durability) can be obtained. When this porous film is used as a separator for batteries, excellent electrolyte impregnability and retaining property can be obtained, and the change in the electric characteristics over time can be reduced.

#### [Characteristic evaluation methods and effect evaluation methods]

In the following, the measurement methods and the evaluation methods used in the present invention will be described.

##### (1) Average pore size

The major and minor axes of the pore size are measured by observing the surface of a sample with a scanning electron microscope (SEM). The combined average of the average major axis and the average minor axis is taken as the average pore size. In this case, if a fibrillar substance (single or multiple types) is present inside the empty pores, it is excluded from the measurement of the average pore size.

## (2) Porosity (Pr)

A sample (10x10 cm) is immersed in liquid paraffin for 24 h. After the liquid paraffin on the surface layer is thoroughly wiped off, the weight ( $W_2$ ) is measured. The empty pore's volume ( $V_0$ ) is derived from the weight ( $W_1$ ) of the sample before it is immersed in liquid paraffin and the density ( $\rho$ ) of the liquid paraffin as follows.

$$V_0 = (W_2 - W_1) / \rho$$

The porosity (Pr) is calculated from the apparent volume (a value calculated from the thickness and size)  $V$  and empty pore's volume  $V_0$ .

$$Pr = V_0 / V \times 100 (\%)$$

## (3) Layer density in the thickness direction

A sample is frozen at the temperature of liquid nitrogen. A cross section is cut out with a microtome along the maximum strength direction. The observation image of the cross section is taken using a scanning electronic microscope (SEM). The brightness and shade (or strength) information of the image is obtained from the observation image at a specific resolution of 0.01-0.03  $\mu\text{m}$  along the thickness direction. The power spectrum is derived by means of high-speed Fourier transform (FFT). The wave number [main wave number ( $\mu\text{m}^{-1}$ )] at the maximum peak of the spectrum (excluding the DC component) is derived. The layer density in the thickness direction at that observation spot is derived as (thickness at the observation spot ( $\mu\text{m}$ ))  $\times$  (the main wave number ( $\mu\text{m}^{-1}$ )). The aforementioned operation is repeated at least 5 times at any measurement spot, and the average is calculated as the layer density in the thickness direction of that sample. The measurement can be facilitated if the SEM magnification rate is in the range of 3000-10,000.

Reference: "Use of FFT" Published by Sanho, 1981.

## (4) Evaluation of hydrophilization

### (a) Wetting index (dyne/cm)

The wetting index was measured according to JIS K6782.

### (b) Wettability with respect to water

After a sample was maintained at an atmospheric temperature of 25°C for 24 h, the sample was placed on a horizontal surface, and distilled water was dropped from a height of 5-20 mm above the sample. The period from the time when the distilled water contacted the surface of the sample to the time when the water penetrated through the surface of the sample to wet the opposite side was measured and graded as follows.

## Judgment

◎: Instantaneous (shorter than 0.5 sec)

O: Longer than 0.5 sec but shorter than 1.0 sec

Δ: Longer than 1.0 sec but shorter than 5.0 sec

x: Longer than 5.0 sec

### (c) Wettability with respect to $\gamma$ -butyrolactone

This property was evaluated in the same way as described in (b) except that  $\gamma$ -butyrolactone was used instead of distilled water.

### (5) Durability of hydrophilization (coating film adhesion)

After a sample was treated in boiling water for 10 h and then dried, the wettability was evaluated in the same way as described in (b) of (4).

### (6) Liquid paraffin penetration time

A liquid paraffin with a viscosity of  $77 \pm 1$  cSt at  $37.8^\circ\text{C}$  as specified in JIS K9003 was used. After the liquid paraffin and a sample were maintained at an atmospheric temperature of  $25^\circ\text{C}$  for 24 h, the sample was placed on a horizontal surface, and 0.03-0.06 g of the liquid paraffin was allowed to drop naturally from a height of 5-20 mm above the sample.

The period from the time when the liquid paraffin contacted the surface of the sample to the time when the liquid paraffin penetrated through the surface of the sample to wet the opposite side was measured as the liquid paraffin penetration time (sec).

### (7) ESR (equivalent serial resistance)

An electrolyte of 3.1 mS/cm was prepared by dissolving triethylamine and phthalic acid in  $\gamma$ -butyrolactone as described in Japanese Kokai Patent Application No. Sho 61[1986]-187221. The DC resistance component of the porous film at 1 kHz in this electrolyte was measured as the ESR ( $\Omega$ ).

In this case, the value ( $2.0 \Omega$ ) of an electrolytic capacitor paper (Manila Paper MER 2.5 50) used as a comparative sample was used as the reference.  $1.7 \Omega$  or lower was graded as O,  $1.8$ - $2.2 \Omega$  was graded as  $\Delta$ , and  $2.3 \Omega$  or higher was graded as x.

The measurement conditions were as follows.

(a) Electrode: Platinum electrode (25 mm square)

Measurement load: 240 g

(b) Impedance measurement device:

AG-4311 LCR Meter (product of Ando Denki K.K.)

Measurement condition: 1 kHz, 5 V range

#### Application examples

In the following, the present invention will be explained in more detail with reference to application examples.

#### Application Example 1

100 parts by weight of a polypropylene powder (product of Mitsui Toatsu Chemicals, Inc., JS type,  $[\eta]=2.4$  dl/g,  $II=97.5\%$ ) used as polyolefin resin and 120 parts by weight of dicyclohexyl phthalate (DCHP, product of Osaka Organic Chemical Industries, Co., Ltd.) were melt-blended and pelletized using a biaxial extruder. Then, the obtained pellets were melt-extruded from a T-die at 210°C using a 40-mm extruder, followed by being fed into a 70°C water tank at a draft ratio (linear gap of the T-die/thickness of the cast film) of 7 for cooling and solidification. As a result, a cast film was obtained. The thickness of the obtained film was 80  $\mu\text{m}$ .

Then, the cast film was fed into a 45°C 1-1-1-trichloroethane extraction tank, where more than 99% of the added DCH was eliminated.

Subsequently, a roll stretching apparatus was used to stretch the film 3.5 times in the length direction at 120°C. The film was then stretched 1.4 times in the width direction using a stenter, followed by 12 sec of thermal fixing at 145°C. The film was then immersed in a 3% ethanol solution of polyoxyethylenenonyl phenyl ether ("Nonypol" 95, product of Sanyo Chemical Industries Ltd.) for 5 sec, followed by 2 min of drying at 100°C.

As shown in Table 1, the film manufactured in this way has excellent hydrophilicity, electrolyte wettability, and hydrophilization durability as well as low ESR and little change in ESR in high-temperature  $\gamma$ -butyrolactone. The film shows excellent characteristics when used as a battery separator.

#### Application Example 2

A cast film was manufactured in the same way as described in Application Example 1, and extraction was carried out in the same way to remove more than 99% of the added DCHP. The film was stretched 2.7 times in the length direction at 125°C using a roll stretching apparatus. Then, the film was stretched 1.3 times in the width direction using a stenter, followed by 12 sec of thermal fixing at 140°C. Also, a mixture consisting of 2 parts of polyoxyethylene alkyl ether ("Emulsion" 70, product of Sanyo Chemical Industries Ltd.) used as surfactant and 1 part of diethanolamine laurate used as the fatty acid amine was dissolved in ethanol to obtain a 3% solution. The aforementioned film was immersed in this solution for 5 sec, followed by



2 min of drying performed at 100°C.

As shown in Table 1, the film manufactured in this way has excellent hydrophilicity, electrolyte wettability, and hydrophilization durability. Like the film obtained in Application Example 1, this film can display excellent electric characteristics and reliability when used as a separator.

### Application Example 3

100 parts by weight of high-density polyethylene (product of Mitsui Petrochemical Co., Ltd., "HI-Zex" 3300] used as polyolefin resin and 110 parts by weight of dicyclohexyl phthalate were melt-blended and pelletized. The obtained pellets were extruded from a T-die at 220°C using a 40-mm extruder, followed by being fed into a 65°C water tank at a draft ratio of 9 for cooling and solidification. As a result, a nonstretched sheet was obtained. The thickness of the obtained sheet was 60  $\mu\text{m}$ . Then, the sheet was fed into a 45°C 1-1-1-trichloroethane extraction tank, where more than 99% of the additive was eliminated. Subsequently, a roll stretching apparatus was used to stretch the sheet 2.5 times in the length direction at 120°C, followed by thermal fixing at 123°C. The film was then immersed in a 3% ethanol solution of a mixture consisting of 2 parts of polyoxyethylenenonyl phenyl ether and 1 part of monoglyceride stearate for 5 sec, followed by 2 min of drying at 100°C.

The evaluation results of the obtained hydrophilized porous film are listed in Table 1. This film has excellent hydrophilicity, electric characteristics, and reliability like the film obtained in Application Example 1.

### Comparative Examples 1, 2, 3

Porous films were manufactured in the same way as in Application Examples 1, 2, and 3 except for omitting the surfactant treatment used in Application Examples 1, 2, and 3. The characteristics of the films are listed in Table 1. All of these films have low wetting tension. Wetting of water and  $\gamma$ -butyrolactone are poor, and the ESR is large.

### Comparative Example 4

A 30- $\mu\text{m}$ -thick film was manufacturing using the same raw material composition as well as the same extruding and casting apparatuses used in Application Example 1.

Then, the film was fed to a 45°C 1-1-1-trichloroethane extraction machine, where more than 99% of the additive DCHP was removed. Then, the film was immersed in a surfactant and dried in the same way as described in Application Example 1.

The characteristics of this porous film are listed in Table 1. When the average porosity is small, wetting of water and  $\gamma$ -butyrolactone becomes poor. The ESR drops after immersing in  $\gamma$ -butyrolactone at 100°C. The long-term reliability is poor.

### Comparative Example 5

Polypropylene with  $[\eta]=1.9$  was used as the polyolefin resin, and water-tank casting (70°C) was performed at a draft ratio of 5 to obtain a 20- $\mu\text{m}$ -thick film from a nozzle set to 210°C. After the film was annealed at 130°C for 5 min, it was stretched 1.75 times at a stretching rate of 100°C/min at 95°C, followed by 3 min of annealing at 135°C. As a result, a porous film was obtained. The film was hydrophilized using a surfactant in the same way as described in Application Example 1. The characteristics of the obtained film are listed in Table 1. The film has a small average pore size and low empty pore rate as well as poor hydrophilization durability and long-term reliability of ESR.

Table 1

	③ 基 材	④ 平均孔径 ( $\mu\text{m}$ )	⑤ 空孔率 (%)	⑥ 厚み方向 層密度	⑦ 親 水 化 評 価			⑪ 親水化の 耐久性	⑫ 膜/バ ッテリ 透過時間 (sec)	⑬ ESR		⑭
					⑧ 濡れ指数	⑨ 水に対する 濡れ性	⑩ $\gamma$ -ブチロラクトン 濡れ性			⑬ 浸漬前	⑬ 浸漬後*3	
①	実施例 1	PP*1	0.7	60	48	58<	○	○	○	1.5	○	○
	2	PP	0.4	65	60	57	○	○	○	2.0	○	○
	3	PE*2	0.8	68	42	58<	○	○	○	1.5	○	○
②	比較例 1	PP	0.7	65	48	30	×	×	—	0.8	×	×
	2	PP	0.4	60	60	30	×	×	—	1.1	×	×
	3	PE	0.8	68	42	31	×	△	—	1.0	×	×
	4	PP	0.03	52	24	56	△	△	△	6.0	△	×
	5	PP	0.02	45	150	58<	△	○	△	3.0	○	×

\*1 Polypropylene

\*2 High-density polyethylene

\*3 Value after immersed in 100°C  $\gamma$ -butyrolactone for 8 h

- Key:
- 1 Application Example \_\_\_\_
  - 2 Comparative Example \_\_\_\_
  - 3 Base material
  - 4 Average pore size
  - 5 Empty pore rate
  - 6 Layer density in the thickness direction
  - 7 Hydrophilization evaluation
  - 8 Wetting index
  - 9 Wettability with respect to water

- 10 Wettability with respect to  $\gamma$ -butyrolactone
- 11 Hydrophilization durability
- 12 Liquid paraffin penetration time
- 13 Before immersion
- 14 After immersion

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Brief description of the figures

Figure 1 shows the crystalline structure on the surface of the hydrophilized polyolefin porous film of the present invention under observation by a scanning electron microscope (total magnification: 10,000).

Figure 2 shows the crystalline structure of the cross section (total magnification: 10,000).



Figure 1



Figure 2